

Effect of Pt substitution on the electronic structure of AuTe₂

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Abstract

We report a photoemission and x-ray absorption study on $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ ($x = 0$ and 0.35) triangular lattice in which superconductivity is induced by Pt substitution for Au. Au $4f$ and Te $3d$ core-level spectra of AuTe_2 suggests a valence state of $\text{Au}^{2+}(\text{Te}_2)^{2-}$, which is consistent with its distorted crystal structure with Te-Te dimers and compressed AuTe_6 octahedra. On the other hand, valence-band photoemission spectra and pre-edge peaks of Te $3d$ absorption edge indicate that Au $5d$ bands are almost fully occupied and that Te $5p$ holes govern the transport properties and the lattice distortion. The two apparently conflicting pictures can be reconciled by strong Au $5d$ /Au $6s$ -Te $5p$ hybridization. Absence of a core-level energy shift with Pt substitution is inconsistent with the simple rigid band picture for hole doping. The Au $4f$ core-level spectrum gets slightly narrow with Pt substitution, indicating that the small Au $5d$ charge modulation in distorted AuTe_2 is partially suppressed.

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I. INTRODUCTION

Layered transition-metal dichalcogenides with triangular motif have been attracting renewed interest due to the discovery of superconductivity in chemically substituted IrTe_2 [1–4] and AuTe_2 [5] with maximum T_c of 3.1 K and 4.0 K, respectively. In particular, the electronic structure of IrTe_2 and its derivatives has been intensively studied using various spectroscopic methods under anticipation that the strong spin-orbit interaction in the Ir $5d$ and Te $5p$ orbitals may provide a novel spin-momentum entangled quantum state. [6–9] Also details of the structural transition in IrTe_2 [10, 11] have been revealed by recent studies using advanced x-ray diffraction and scattering techniques. [12–16] On the other hand, so far, electronic structure studies on AuTe_2 and its derivatives are limited although the Au $5d$ and/or Te $5p$ electrons with strong spin-orbit interaction can provide an interesting electronic state.

AuTe_2 is known as a natural mineral Calaverite with monoclinically distorted CdI_2 -type layered structure (space group C2/m). [17] Each Au-Te layer contains edge-shared AuTe_6 octahedra which are strongly distorted with two short (2.67 Å) and four long (2.98 Å) Au-Te bonds due to Te-Te dimer formation in the average structure. [17, 18] A detailed analysis of the crystal structure has revealed the incommensurate structural modulation which may indicate charge ordering of Au $5d$ and/or Te $5p$ valence electrons. [19] Although $\text{Au}^+/\text{Au}^{3+}$ charge disproportionation has been suggested to explain the structural distortion, [19] the expected Au valence modulation has not been detected by x-ray photoemission spectroscopy. [20] In addition, *ab-initio* calculations have indicated that the Au $5d$ subshell is almost fully occupied by electrons and the Te-Te dimer formation due to the partially occupied Te $5p$ subshell should be responsible for the structural distortion. [21] Very recently, Kudo *et al.* have found that Pt substitution for Au suppresses the lattice distortion of AuTe_2 and that $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ with undistorted CdI_2 -type ($\text{P}\bar{3}\text{m1}$) structure exhibits superconductivity with maximum T_c of 4.0 K. [5] The electronic phase diagram for $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ is similar to $\text{Ir}_{1-x}\text{Pt}_x\text{Te}_2$, indicating intimate relationship between the lattice distortion in AuTe_2 and the superconductivity in $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$. In the present work, we have studied the fundamental electronic structure of $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ ($x=0$ and 0.35) by means of ultra-violet photoemission spectroscopy (UPS), x-ray photoemission spectroscopy (XPS), and x-ray absorption spectroscopy (XAS). The valence-band UPS and XPS results show that the Au $5d$ and Te $5p$

orbitals are strongly hybridized near the Fermi level. The core-level XPS results indicate small charge distribution of the Au $5d$ electrons which is suppressed by the Pt substitution. Active role of the Te $5p$ holes is indicated by the Te $3d$ XAS measurement.

II. EXPERIMENTS

The polycrystalline samples of $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ ($x=0.35$, $T_c=4.0$ K) and single crystals of AuTe_2 were prepared as reported in the literature. [5] Single crystals of AuTe_2 were cleaved for UPS and XAS at 300 K. UPS measurements were performed at UBC using SPECS Phoibos 150 analyzer with the He I line (21.2 eV) from a monochromatized UVS300 lamp. The total energy resolution was set to 25 meV. The base pressure was in the 10^{-11} mbar range. XAS measurements were performed at beamlines 11ID-1 and 10ID-2 [22], Canadian Light Source. The total-energy resolution was 100 meV. The base pressure of the XAS chamber was in the 10^{-9} mbar range. The spectra were measured in the total-electron-yield (TEY) mode. XPS measurements were carried out using JEOL JPS9200 analyzer. Mg $K\alpha$ (1253.6 eV) was used as x-ray source. The total energy resolution was set to ~ 1.0 eV, and the binding energy was calibrated using the Au $4f$ core level of the gold reference sample at 84.0 eV. The polycrystalline sample of $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ ($x=0.35$) and single crystal of AuTe_2 were fractured *in situ* at 300 K for the XPS measurements.

III. RESULTS AND DISCUSSION

Figure 1 shows the Au $4f$ core-level spectra of $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ ($x=0$ and 0.35) taken at 300 K, which are compared with $\text{Cs}_2\text{Au}_2\text{Br}_6$ with Au^+ and Au^{3+} sites. The broad Au $4f_{7/2}$ peak of AuTe_2 would be consistent with the Au valence modulation due to the lattice distortion. However, the Au $4f_{7/2}$ peak width of $\text{Au}_{0.65}\text{Pt}_{0.35}\text{Te}_2$ without the distortion is also comparable to that of AuTe_2 . While the formal valence of Au is +4 in $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$, the Au $4f_{7/2}$ peaks are slightly higher in binding energy than that of pure Au (84.0 eV) and located between the Au^+ and Au^{3+} peaks of $\text{Cs}_2\text{Au}_2\text{Br}_6$, suggesting that the actual average Au valence in $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ is close to $2+$. Although the Au^{2+} ion is expected to take the $5d^9$ configuration, the band-structure calculations on the average structure indicate that the Au $5d$ bands are almost fully occupied. [21, 24]

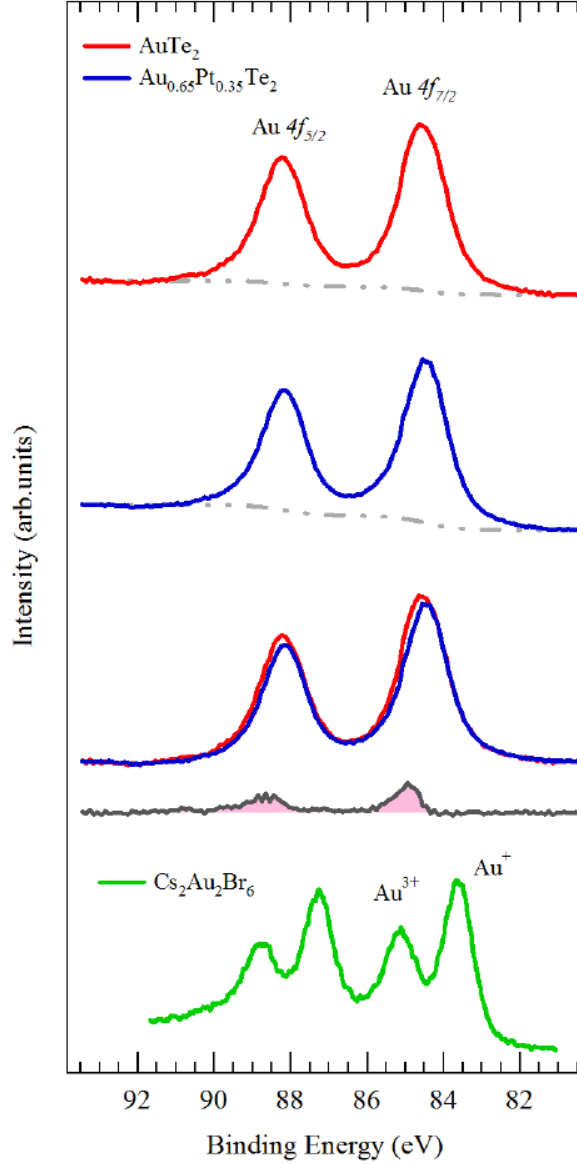


FIG. 1: (color online) Au $4f$ core-level XPS spectra of AuTe_2 and $\text{Au}_{0.65}\text{Pt}_{0.35}\text{Te}_2$ compared with $\text{Cs}_2\text{Au}_2\text{Br}_6$. [23] The dash-dot curves indicates backgrounds due to secondary electrons. The background subtracted spectra of $\text{Au}_{0.65}\text{Pt}_{0.35}\text{Te}_2$ is overlaid with that of AuTe_2 , and the difference spectrum between the background-subtracted spectra is indicated by the solid curve with shaded peak area.

The Te $3d$ core-level spectra of $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ ($x=0$ and 0.35) are displayed in Fig. 2. The binding energy of the Te $3d_{5/2}$ core level is close to that of pure Te (573.0 eV), [25] suggesting that the Te $5p$ orbitals are not fully occupied and contribute to the electronic states at the Fermi level. The shoulder structures located at ~ 576 eV and ~ 587 eV for Te $3d_{5/2}$ and

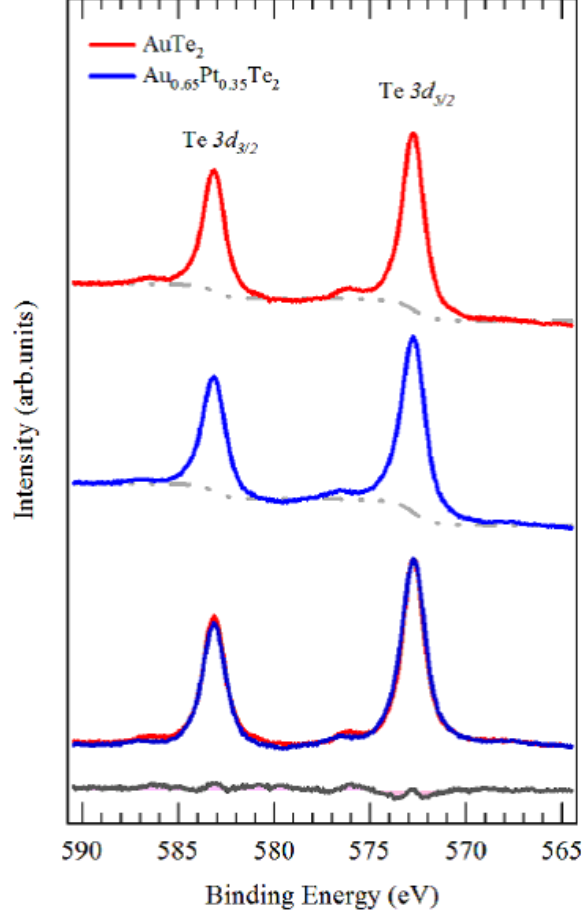


FIG. 2: (color online) Te $3d$ core-level XPS spectra of AuTe_2 and $\text{Au}_{0.65}\text{Pt}_{0.35}\text{Te}_2$. The dash-dot curves indicates background due to secondary electrons. The background subtracted spectra of $\text{Au}_{0.65}\text{Pt}_{0.35}\text{Te}_2$ is overlaid with that of AuTe_2 , and the difference spectrum between the background-subtracted spectra is indicated by the solid curve with shaded peak area.

Te $3d_{3/2}$ are derived from Te oxide contaminations which were also observed in the IrTe_2 single crystals and the $\text{Ir}_{1-x}\text{Pt}_x\text{Te}_2$ polycrystalline samples. [6] The shoulder structures in the AuTe_2 single crystal and the polycrystalline $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ are much smaller than that in the polycrystalline $\text{Ir}_{1-x}\text{Pt}_x\text{Te}_2$ and are as small as that in the high quality IrTe_2 single crystal, indicating that the surface quality of AuTe_2 and $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ is reasonably good.

In order to clarify the effect of Pt substitution, we have subtracted the core-level spectrum of $\text{Au}_{0.65}\text{Pt}_{0.35}\text{Te}_2$ from that of AuTe_2 as displayed in Figs. 1 and 2. The Au $4f$ and Te

3d core-level peaks do not show appreciable energy shift with the Pt substitution. The difference spectrum shows that the Au 4f core-level spectrum of AuTe₂ gets slightly narrow with the Pt substitution, while it does not affect the Te 3d core level appreciably. This indicates small Au 5d charge modulation in distorted AuTe₂ and partial suppression of the charge modulation by the Pt substitution. Here, one cannot fully exclude the possibility that the Au valence at the surface is different from the bulk and that the surface component is enhanced in AuTe₂. However, the surface condition of the AuTe₂ single crystal is expected to be better than Au_{0.65}Pt_{0.35}Te₂, and the surface component in AuTe₂ should be smaller than the polycrystalline case if it exists. On the other hand, the Au 4f peak is broader in the AuTe₂ single crystal than the polycrystalline case. Therefore, it is natural to assign the extra broadening in AuTe₂ to the extra charge modulation instead of the surface effect.

In Fig. 3, valence-band XPS and UPS spectra of Au_{1-x}Pt_xTe₂ (x=0 and 0.35) taken at 300 K are displayed. The valence-band UPS and XPS spectra of Au_{1-x}Pt_xTe₂ show several structures. The broad structures ranging from 0 to 4 eV below the Fermi level can be assigned to the Te 5p orbitals (mixed with the Au 5d/6s orbitals) on the basis of the band-structure calculations on AuTe₂. [21, 24] The structures from 4.0 to 6.5 eV can be assigned to the Au 5d bands since it gains spectral weight in going from UPS to XPS, as expected from the photon energy dependence of the photoionization cross-section of Au 5d relative to Te 5p. Indeed, the valence-band spectra are consistent with the calculated density of states [24] in which the Au 5d bands are located in the region from 4.0 eV to 6.0 eV below the Fermi level. The valence-band spectra of Au_{0.65}Pt_{0.35}Te₂ is shifted toward lower binding energy, indicating that the Pt substitution for Au may correspond to hole doping to the Te 5p bands mixed with the Au 5d/6s orbitals. Another possibility is that mixing of the Au 5d bands with the Pt 5d bands leads to the energy shift of the Au/Pt 5d bands since the Pt 5d bands are expected to have lower binding energy than the Au 5d bands. The absence of the core-level energy shift is inconsistent with the former scenario (hole doping in a rigid band manner) and supports the latter scenario. Namely, the Pt substitution changes the shape of the valence band constructed from the Au/Pt 5d/6s and Te 5p orbitals, and it cannot be viewed as a simple hole doping to AuTe₂ in a rigid band manner.

The average Au valence close to +2 and the unoccupied Te 5p orbitals indicate that the charge-transfer energy from the Te 5p orbitals to the Au 5d orbitals is negative to stabilize the valence state of Au²⁺(Te₂)²⁻. Namely, the local electronic configuration of the AuTe₆

octahedron is close to $d^9\bar{\text{L}}^2$ ($\bar{\text{L}}$ represents a ligand hole in the Te $5p$ orbitals) instead of d^7 . Therefore, each Te site accommodates approximately one hole, and the Te $5p$ holes govern the transport properties and the lattice distortions in AuTe_2 . This picture is consistent with the Te-Te dimers in AuTe_2 since the antibonding molecular orbital of the Te-Te dimer can be occupied by the two Te $5p$ holes from the two Te sites. On the other hand, the band-structure calculations on AuTe_2 with the average structure [21, 24] as well as the valence-band spectra indicate that the Au $5d$ bands are almost fully occupied. In order to resolve this apparent paradox, strong hybridization between the Au $5d/6s$ and Te $5p$ orbitals should be taken into account. Starting from the $\text{Au}^{2+}(\text{Te}_2)^{2-}$ valence state, the hybridization between the Au $5d/6s$ orbitals and the Te-Te bonding and antibonding molecular orbitals can induce additional charge transfer. Since the Au $5d$ level in AuTe_2 is much lower than the Ir $5d$ level in IrTe_2 , charge donation from the Te-Te bonding orbital to the Au $5d$ orbitals can be dominant in AuTe_2 whereas back donation from the Ir $5d$ orbitals to the Te-Te antibonding orbital would be substantial in IrTe_2 . In addition, the Au $6s$ component can be mixed into the Au $5d$ bands through the strong Au $5d$ -Te $5p$ and the Te $5p$ -Au $6s$ hybridizations. Therefore, although the "Au $5d$ bands" constructed from the atomic Au $5d$, Au $6s$, and Te $5p$ orbitals are fully occupied as predicted by the band-structure calculations and observed by the valence-band photoemission experiments, actual number of atomic Au $5d$ electrons in AuTe_2 can remain close to nine which is consistent with the $\text{Au}^{2+}(\text{Te}_2)^{2-}$ valence state. The d^9 configuration of Au^{2+} is consistent with the Jahn-Teller like distortion of the AuTe_6 octahedra with two short and four long Au-Te bonds.

Figure 4 shows the Te $3d$ XAS spectrum of $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ ($x=0$ and 0.35). The pre-edge and main edge structures are clearly observed. The main-edge structure corresponds to transition from the Te $3d$ core level to the unoccupied Te $4f/\text{Au } 6s, 6p$ states. On the other hand, the pre-edge structure can be assigned to the transition from the Te $3d$ core level to the Te $5p$ orbitals, indicating that the Te $5p$ bands cross the Fermi level and that the Te $5p$ holes play essential roles in the transport properties. This Te $5p$ -hole picture is consistent with the XPS and XAS results. In AuTe_2 , the Te $5p$ orbitals are partially unoccupied, and the bond formation by the Te $5p$ holes creates the Te-Te dimers. The Te-Te dimer formation leads to the long and short Te-Te bonds, [17, 18] which can induce charge modulation of Au through the strong hybridization between the Au $5d$ and Te $5p$ orbitals. On the other hand, since all the Te sites belong to one of the Te-Te dimers, each Te site accommodates

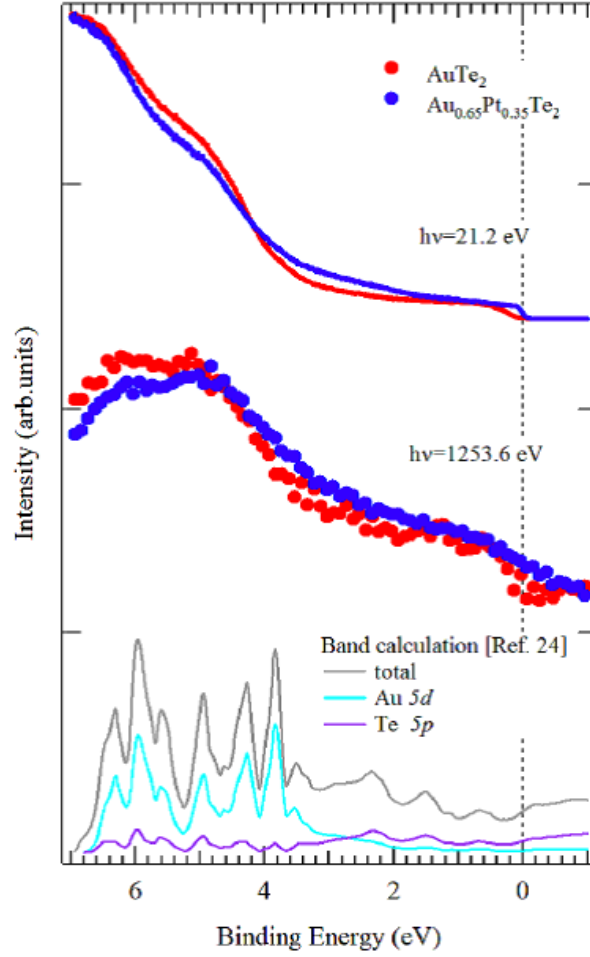


FIG. 3: (color online) Valence-band UPS and XPS spectra of AuTe_2 and $\text{Au}_{0.65}\text{Pt}_{0.35}\text{Te}_2$ compared with the total and partial density of states of AuTe_2 . [24]

almost same amount of Te $5p$ hole. When Pt is substituted for Au in $\text{Au}^{2+}(\text{Te}_2)^{2-}$, Pt ions tend to be $3+$ or $4+$ and supply electrons to Te-Te antibonding orbitals. Consequently, the local Te-Te dimers are partly broken around the Pt sites, and the superstructure due to the short Te-Te bond (intradimer) and long Te-Te bond (interdimer) is strongly disturbed. In this scenario, disordered local Te-Te dimers can remain in $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$. The remaining Au charge fluctuation and the disordered Te-Te dimers may provide anomalous lattice behaviors to $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ and may contribute to the emergence of superconductivity. [5]

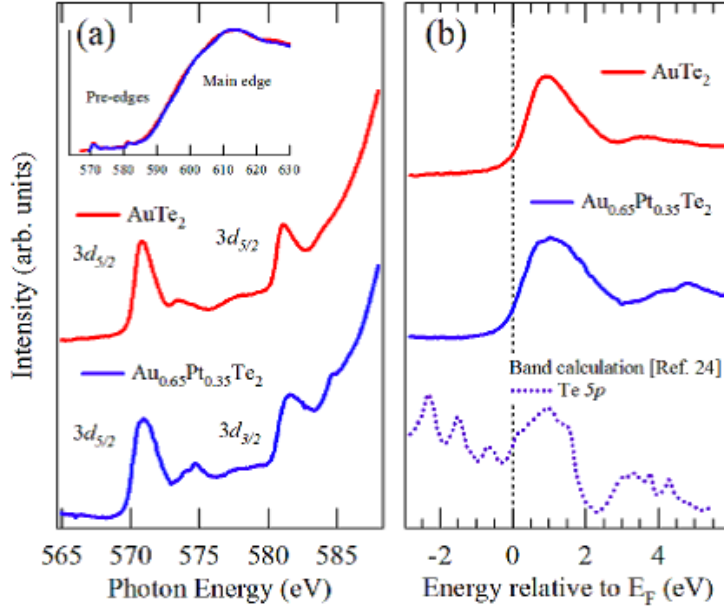


FIG. 4: (color online) (a) Te 3d XAS spectrum of AuTe_2 and $\text{Au}_{0.65}\text{Pt}_{0.35}\text{Te}_2$. The inset shows the wide-range XAS spectrum including the main edge. (b) The Te $3d_{5/2}$ XAS spectrum is compared with the calculated density of states. [24] Here, it is assumed that the Fermi level is roughly located around the absorption edge.

IV. CONCLUSION

We have performed photoemission and x-ray absorption measurements on $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ ($x=0$ and 0.35) in which the Pt substitution for Au suppresses the lattice distortion in AuTe_2 and induces the superconductivity. The broad Au $4f$ core-level peak is consistent with the Au valence modulation in distorted AuTe_2 . The Au $4f$ core-level peak gets slightly narrow with the Pt substitution, indicating that small Au $5d$ charge modulation in distorted AuTe_2 is at least partially suppressed by the Pt substitution. The Au $4f$ and Te $3d$ core-level binding energies suggest that average valence state is close to $\text{Au}^{2+}(\text{Te}_2)^{2-}$ consistent with the Jahn-Teller like distortion of the AuTe_6 octahedra. On the other hand, the valence-band spectra and the band-structure calculations show that the Au $5d$ bands are almost fully occupied. The two apparently conflicting results can be reconciled by taking account of the strong Au $5d$ /Au $6s$ -Te $5p$ hybridization. The absence of core-level energy shift with the Pt substitution shows that the simple rigid band picture is not applicable to $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$. Although the periodic arrangement of the Te-Te dimers is disturbed by the Pt substitution, the Te-Te

dimers and Au valence modulation may partly remain in superconducting $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$. The relationship between the possible Au charge fluctuation and the superconductivity should be studied experimentally and theoretically in future. Another interesting question is that the Te-Te dimers still remain in $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ or not. If the Pt substitution causes disordering of the dimers instead of breaking, $\text{Au}_{1-x}\text{Pt}_x\text{Te}_2$ should have highly inhomogeneous electronic states similar to the Fe-based superconductors.

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